ICASE

IMPROVED CI FORMULA EVALUATION:

THE ELIMINATION OF THE PHASE DETERMINATION

AT THE DETERMINANT LEVEL FOR ARBITRARILY COUPLED CSF'S

Charles W. Bauschlicher, Jr.

ICASE REPORT NO. 79-25

September 20, 1979

INSTITUTE FOR COMPUTER APPLICATIONS IN SCIENCE AND ENGINEERING

NASA Langley Research Center, Hampton, Virginia

Operated by the

UNIVERSITIES SPACE USRA RESEARCH ASSOCIATION

IMPROVED CI FORMULA EVALUATION:
THE ELIMINATION OF THE PHASE DETERMINATION
AT THE DETERMINANT LEVEL FOR ARBITRARILY COUPLED CSF'S

By

Charles W. Bauschlicher, Jr.

Institute for Computer Applications in Science and Engineering

ABSTRACT

A method for eliminating the phase determination at the determinant level for arbitrarily coupled CSF's is presented.

This report was prepared as a result of work performed under NASA Contracts No. NAS1-14101 and NAS1-14472 while in residence at ICASE, NASA Langley Research Center, Hampton, VA 23665.

In a conventional Configuration Interaction (CI) calculation (for a general reference on CI, see reference 1.), the n-particle basis functions are normally linear combinations of Slater determinants having the correct overall spin and space symmetry, called configuration state functions (CSF). After choosing a list of CSF's to be included in the CI calculation, the matrix elements between these CSF's must be evaluated.

The basis steps involved in the matrix element evaluation are: two orbital occupations are compared, if the difference is greater than two the matrix element is zero; if the difference is two or less, the matrix element is non-zero and evaluated. The evaluation is accomplished by expanding all CSF's arising from occupation 1 or occupation 2 into determinants. The evaluation of the determinant(occupation 1)-determinant(occupation 2) interactions is accomplished using the Slater-Condon[2,3] rules. The matrix elements over determinants are then transformed to matrix elements over CSF's. While the evaluation of matrix elements over determinants is formally very simple, the need to determine the phase associated with bringing the determinants into maximum coincidence can be very time consuming.

Several methods for reducing the amount of work needed to compute matrix elements between CSF's have been developed (see reference 1 and the references therein). All of these methods rely on using specific full couplings of the determinants to form CSF's. In some of these schemes one need never explicitly consider determinant-determinant interactions. However, if the interacting space[4-6] is used instead of the full coupling space, the number of CSF's is reduced and correspondingly, the work needed to construct (if a formula tape is used) and diagonalize the H matrix is reduced. This reduction in work comes with virtually no loss in accuracy[6]. Ironically a program which is general enough to use the interacting space, will probably

take longer to evaluate the H-matrix formula, using the interacting space, than a special purpose program using the full space arising from the same occupations. Davidson[7] has noted that this difference in time can be so great as to make the interacting space undesirable. Liu[8] has pointed out that while the formula evalution might be slower, the reduction in external storage, and in IO and CPU time for the H-matrix construction and diagonalization can make the use of interacting space desirable overall, especially if using a formula tape and computing many points.

The use of the interaction space can be made more desirable if the phase determination is moved to the occupational level as with the full coupling methods. Lengsfield[9] developed such a method which was suitable for occupations differing by one, and used this in the calculation of transition moments. Unfortunately, this method was not easily extendable to differences of two. Here we present a general method for eliminating the phase at the determinant level for arbitrary couplings.

Starting with an occupation written as follows,

$$1\alpha \;\; 1\beta \;\; 2\alpha \;\; 2\beta \;\; 4\alpha \;\; 4\beta \;\; 3 \;\; 7 \;, \qquad (1)$$

where 3 and 7 are open shells and can have different spins in different determinants, the closed shell α orbitals are moved to one end and put in ascending order, while the β closed shell orbitals and the open shell orbitals are put in ascending order:

$$1\beta \;\; 2\beta \;\; 3 \;\; 4\beta \;\; 7 \qquad 1\alpha \;\; 2\alpha \;\; 4\alpha \;. \qquad (2)$$

The phase of going from 1 to 2 is determined. In this order the two parts of 2 can easily be represented as bit patterns. For 60 orbitals or less we use 3 words, one to hold the β closed and open shell occupations, a second to hold the α closed shell orbitals, and a third word is used to hold the phase, a pointer indicating which spin coupling table describes how to couple

the open shell orbitals, and a list of the open shell orbitals. Actually, when the number of open shells is large, additional words are needed for the list.

For a given occupation, we loop over all previous occupations. For a difference of one or two we go to special code to evaluate the matrix elements. From the orbital difference at the occupation level, a list of all possible integrals which might be needed can be prepared. The orbital non-coincidences are moved to one end, put in ascending order, and the phase of this lineup is determined. We call this the α phase.

The following is an example of a difference by two:

1β	2β	3	4β	7			1α	2α	4α	occupation 1
1β	2β		4β	7	10	11	1α	2α		occupation 2

The orbital non-coincidences are 3 4 and 10 11.

3	4α		1β	2β	4β	7	1α	2α
10	11		1β	2β	4β	7	1α	2α

The α phase is -1 (ignoring the initial phases).

In this scheme whenever an orbital non-coincidence arises from an open to closed or closed to open excitation, we bring down the α closed orbital, but the difference at the determinant level might be the β closed shell orbital. The phase of switching all these open-closed and closed-open orbitals to a difference of the β closed orbital is determined and called the β phase. In the example, this would involve orbital 4 (or one switch 4α with 4β) or β phase of $-\alpha$ phase.

The determinants are stored as bit patterns in an α word and a β word. We loop over the determinants of occupation 1 and loop over the determinants of occupation 2. We 'exclusive or' the α words and the β

words and count the populations. A difference of 4α implies that whenever an orbital changed from open to closed or closed to open the difference was the α orbital so the matrix element is α phase*(direct-exchange). A 4β difference implies that for all open to closed or closed to open orbitals the difference is the β closed orbital and the matrix element is β phase*(direct-exchange). For $2\alpha 2\beta$ difference we must ask how many of the β differences came from open to closed or closed to open orbitals. This is accomplished by having a word with a bit on for each open to closed or closed to open orbital. This word is 'and'ed' with the β difference word and the population (p) is determined. The $2\alpha 2\beta$ phase is then α phase*-1^p. A simple test separates the matrix element into either a direct term ($2\alpha 2\beta$phase*direct) or an exchange term ($-2\alpha 2\beta$phase*exchange). The occupational difference of one is treated in a similar manner.

We should note that since no phase work is performed on the determinants, there is no need to form and phase all of the determinant bit patterns at the beginning of the calculation, but instead, we form the determinants as needed from the α closed word, the list of open shells and the spin coupling table. Our storage is only about 3 words per occupation (for 60 orbitals or less), plus 4 times the maximum number of determinants in a CSF and the scratch space needed to evaluate the matrix elements.

We have presented a method of reducing the amount of work needed to generate a CI formula for arbitrarily coupled determinants. This scheme makes the use of the interacting space more desirable, since the formula evaluation should be comparable if not faster, than a special purpose full coupling program, and since the external storage and IO and CPU time required for the construction and diagonalization of the H-matrix has been reduced. The other advantages of this method are the small amount of memory required, and the relaxation of the limit on the number of open shells, and of the restriction on the couplings.

References

1. I. Shavitt, Modern theoretical Chemistry, Vol.III, Methods of Electronic Structure Theory, Ed. H. F. Schaefer,III. New York, Plenum Press 1977.
2. J. C. Slater, Phys. Rev. 34, 1293 (1929).
3. E. U. Condon and G. H. Shortley, The Theory of Atomic Spectra, Cambridge U.P., London (1935).
4. A. Bunge, J. Chem. Phys. 53, 20 (1970).
5. A. D. McLean and B. Liu, J. Chem. Phys. 58, 1066 (1973).
6. C. F. Bender and H. F. Schaefer III, J. Chem. Phys. 55 4798 (1971).
7. E.R. Davidson, private communication.
8. B. Liu, private communication.
9. B. H. Lengsfield, private communication.